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Selective Dehydrogenation of Propane Over Novel Catalytic Materials

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Abstract

The conversion of small alkanes into alkenes represents an important chemical processing area; ethylene and propylene are the two most important organic chemicals manufactured in the U.S. These chemicals are currently manufactured by steam cracking of ethane and propane, an extremely energy intensive, nonselective process. The development of catalytic technologies (*e.g.*, selective dehydrogenation) that can be used to produce ethylene and propylene from ethane and propane with greater selectivity and lower energy consumption than steam cracking will have a major impact on the chemical processing industry. This report details a study of two novel catalytic materials for the selective dehydrogenation of propane: Cr supported on hydrous titanium oxide ion-exchangers, and Pt nanoparticles encapsulated in silica and alumina aerogel and xerogel matrices.

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Selective Dehydrogenation of Propane over Novel Catalytic Materials

Introduction

Ethylene and propylene comprise the two most important organic feedstocks manufactured by U.S. industry. These two chemicals are currently manufactured by steam cracking of ethane and propane, an extremely energy intensive process that consumes approximately 1.4 quads/yr for ethylene and 0.7 quads/yr for propylene [1]. Steam cracking also suffers from selectivity problems, producing by-products that lower yields. The development of catalytic technologies (*e.g.*, selective dehydrogenation) that produce ethylene and propylene with greater selectivity and lower energy consumption could therefore have a profound effect on the competitiveness of the U.S. chemical industry. Although catalytic dehydrogenation is practiced commercially for larger alkanes (*e.g.*, ethylbenzene, butanes), ethylene and propylene are not currently produced by this route. There are two major reasons for this absence of commercial light alkane dehydrogenation processes: 1) methyl C-H bonds are stronger than methylene C-H bonds, making dehydrogenation more endothermic for light alkanes than heavy alkanes and necessitating higher reaction temperatures to achieve practical conversions, and 2) catalysts that remain selective at the temperatures required for good conversion of light alkanes have not been developed.

This report details the synthesis and catalytic activity of two novel classes of materials for the selective dehydrogenation of propane. The first material is based on hydrous titanium oxide (HTO) ion-exchange materials [2]. HTO materials, formed by the hydrolysis of a titanium alkoxide in the presence of NaOH, possess high intrinsic ion-exchange capacities and thereby allow high loadings of catalytically active metals to be achieved with atomic dispersion. This property results in more efficient utilization of active metals than other catalyst preparation techniques. For example, for both ethylbenzene and isobutane dehydrogenation, Fe/HTO and Cr/HTO catalysts demonstrate higher activities per active metal atom than the best available commercial catalysts [3]. This earlier work with Cr/HTO catalysts for isobutane dehydrogenation was limited to a narrow range of metal loadings. In this work we extend the results for Cr/HTO catalysts to a much wider range of metal loadings and to the propane dehydrogenation reaction.

The high specific activities achieved in the earlier studies of Cr/HTO and Fe/HTO catalysts indicate that high metal dispersion is a very desirable property for selective dehydrogenation catalysts, provided this dispersion can be achieved with metal loadings high enough to result in good overall conversions. This conclusion led to a search for other novel materials that might possess the capability of effectively dispersing relatively high loadings of metals within an oxide support matrix. A review of Sandia's materials capabilities led to the identification of aerogel and xerogel encapsulated metal nanoclusters as potential active catalysts for propane dehydrogenation. Metal nanoclusters are synthesized by the chemical reduction of metal salts solubilized in an organic medium through the use of surfactants. If this reduction is carried out in the presence of an alumina or silica sol, followed by gelation of the sol to form an aerogel or xerogel, the metal particles become encapsulated inside the gel, forming a supported metal catalyst. Provided the pore sizes within the gels are small enough, diffusion and sintering of the

metal particles during high temperature reaction is inhibited, thereby maximizing metal dispersion, activity and stability. In this work we have studied a series of Pt particles encapsulated in both silica and alumina aerogels and xerogels.

Experimental

HTO supports were prepared using the method of Dosch *et al.* [2]. In all cases, the Na:Ti ratio was adjusted to a value of 1:2 to maximize ion-exchange capacity. Also, tetraethyl orthosilicate (TEOS) was added to give a Si:Ti ratio of 1:5. The presence of silica greatly stabilizes support surface area during high temperature reaction. Chromium was loaded onto the HTO supports by first equilibrating the HTO material at a desired pH using HCl, then adding a solution of the metal salt (0.12 M Cr(NO₃)₃) containing a two to three-fold excess of metal with mild stirring. After one hour, the ion-exchanged HTO was filtered, washed with water and acetone, and dried under vacuum at room temperature. The resulting material was then analyzed for metal content by atomic absorption, and BET surface areas were measured.

Pt clusters were encapsulated into silica and alumina aerogels and xerogels using the following procedure. The surfactant didodecyldimethylammonium bromide (DDAB) was added to toluene to form a 5 wt% solution. A sufficient quantity of PtCl₂ was then added to the surfactant solution to result in a 0.005 M Pt concentration. Next, the gel precursor (tetraethyl orthosilicate or a 1:1 molar ratio solution of aluminum tri-*sec*-butoxide and ethyl acetoacetate)) was added to the DDAB/Pt/toluene solution. For the silica materials a 23:1 molar ratio of toluene:precursor was used, while for the alumina materials, a 14:1 molar ratio was used. A 2M solution of LiBH₄ in tetrahydrofuran was then added in sufficient quantity to ensure a three fold excess of LiBH₄ relative to Pt. Finally, for the silica samples an aqueous solution of tetrabutylammonium hydroxide (TBAOH, 40 wt% in water) was added so that the molar ratio of water to silicon was 3:1, while for the alumina samples a 4.3 M aqueous solution of nitric acid was added so that the molar ratio of water to alumina was 3:1. The resulting sol-gel solutions were aged for one week at 50°C, and then washed twice with hexane and dried in air at 40, 50, and 120°C to form xerogels, or subjected to super critical extraction in CO₂ at 40°C to form aerogels.

In addition to the four samples resulting from the procedure described above, a fifth sample was formed by separate synthesis of the nanoclusters and silica. First, Pt clusters were formed by reduction of the Pt salt with LiBH₄ in a DDAB/toluene solution with no gel monomer present. Separately, a silica gel monolith was formed by standard procedures in using ethanol as a solvent [5]. A series of three solvent washes replaced the ethanol with toluene after formation of the monolith. Finally, the cluster solution was poured over the monolith, and the clusters allowed to diffuse into the micropores of the silica. The sample was then dried under ambient conditions as described above for the Pt/silica xerogel. This sample is designated Pt/silica xerogel* in order to distinguish it from the previous Pt/silica xerogel sample. All samples were analyzed for Pt content by atomic absorption.

All samples were initially in the form of a single monolithic piece. These monoliths were carefully ground and sieved to obtain a -60/+80 mesh fraction for use in reactor testing. The remainder of the sample disintegrated into a fine powder which was used for the majority of the physical characterization (see below). The Pt/silica xerogel* sample was tested for propane

dehydrogenation in the powdered state since careful grinding of the monolith did not result in a sufficient quantity of -60/+80 mesh material.

Activity measurements were made in a fixed bed flow reactor shown schematically in Figure 1. Gases are fed through calibrated mass flow controllers and up to two gases can be fed at any time (only one mass flow controller is shown in the figure for clarity). The system is also capable of handling liquid feeds, but this capability was not used here. The reactants enter a high temperature oven, and are preheated and mixed (if multiple feeds are used) in a 1/8" coiled stainless steel tube at the reactor inlet. The preheated reactants then enter a 3/8" stainless steel tube containing catalyst. The catalyst is supported on a fine steel mesh located at the bottom of the reactor. Depending on catalyst density, 2-4 g of catalyst are typically used to give a catalyst bed volume of 3.6 cc. After exiting the reactor, product gases are exhausted through the sample loop of a gas chromatograph, where C1-C4 hydrocarbons are analyzed. Reactor temperature is measured by three thermocouples externally attached to the top, middle, and bottom of the reactor, and one thermocouple located inside the reactor at the bottom of the catalyst bed. No significant differences are ever observed among the four thermocouples indicating that the reactor operates in an isothermal mode. In addition to the Cr/HTO and Pt catalysts, a commercial 7.5 wt% Cr/ γ -Al₂O₃ catalyst was also tested as a benchmark.

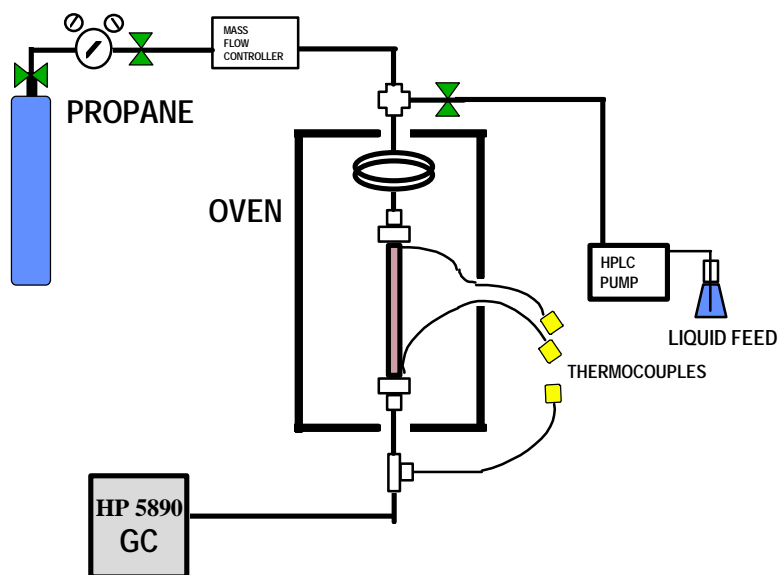


Figure 1: Schematic Diagram of Dehydrogenation Reactor

A typical reaction sequence begins with heating of the catalyst bed to reaction temperature (typically 525-575°C) in flowing nitrogen. Once temperature is reached, the nitrogen flow is stopped and reactant flow begun. A pure propane feed was used as the reactant stream in all experiments. Gas sampling and analysis was performed at 20 minute intervals. For the Pt catalysts, reduction treatments in pure hydrogen were often found necessary to activate the catalysts. For both the Cr/HTO and Pt catalysts, air oxidation was used to regenerate the catalysts at periodic intervals. After completion of a reaction sequence, the reactant flow is shut

off and the reactor is cooled to room temperature in flowing nitrogen. After conclusion of the reactor test, the catalyst is removed from the reactor and saved for BET analysis.

RESULTS AND DISCUSSION

Chromium/HTO Catalysts

Chromium Loading

Figure 2 shows the chromium loading vs. pH for the four samples studied here. Note that the loadings are substantially higher than those reported previously [3], due to an earlier error in the Cr analysis procedure. We believe that the loadings reported here are correct. The Cr loading increases in a quasi-linear fashion with loading pH. Cr loading varies by nearly a factor of two over the range of pH studied.

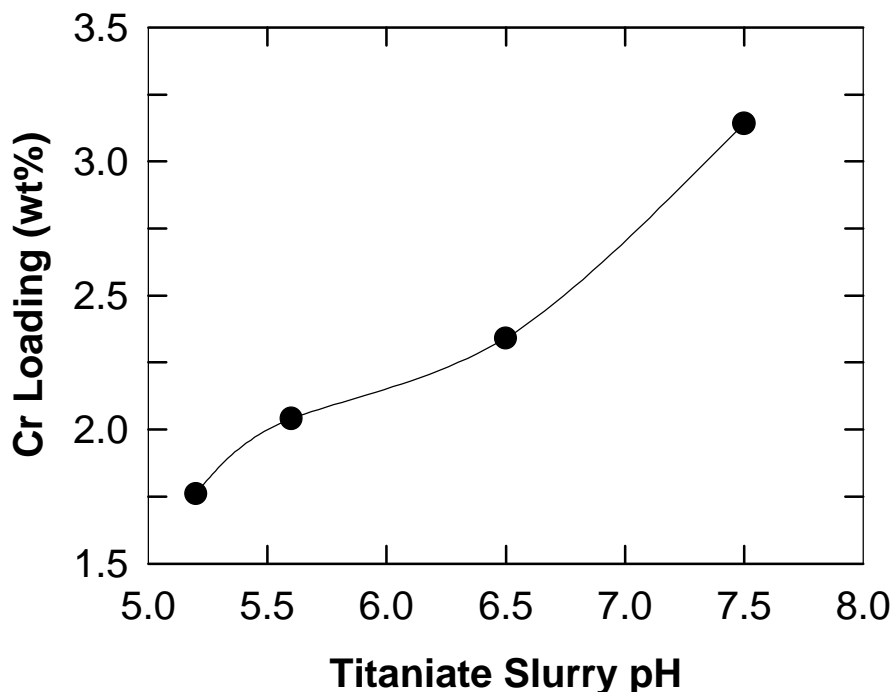


Figure 2: Variation of Chromium Loading on HTO Supports with pH of Ion-Exchange Solution

Propane Dehydrogenation

Figure 3 shows the propane dehydrogenation activity of the Cr/HTO catalysts at 500°C with a weight hourly space velocity (WHSV) of 1.8 h⁻¹. Selectivities to propylene of 97-98% were achieved for all Cr/HTO catalysts. The data show that the Cr loading has very little effect on conversion over the range of loadings studied. Activity measurements for isobutane dehydrogenation over the same catalysts (not reported here) also shows this same insensitivity to Cr loading. A blank experiment with no catalyst in the tube indicates that the conversions

measured are due to the presence of a catalyst and not to thermal reactions or reaction occurring on the reactor tube walls. The reasons for the insensitivity to Cr loading are not at all clear. In the case of Fe/HTO catalysts for ethylbenzene dehydrogenation [3,4] a very sharp maximum in activity with iron loading is observed at a loading of ~1.6 wt%. This maximum was attributed to the formation of a particular ion-exchanged iron species that only forms within a very narrow pH window during ion-exchange. The fact that the *overall* activity of Cr/HTO catalysts is insensitive to Cr loading suggests that *specific* activity (conversion/g Cr) of Cr loaded at low pH is greater than that of Cr loaded at high pH. This behavior could either be the result of differences in the chemical state of the Cr loaded at different pH values, as postulated for Fe/HTO catalysts, or due to the formation of larger Cr particles at higher pH, which would offset the effects of higher Cr loadings. Transmission electron microscopy (TEM) could shed light on this issue. Nevertheless, the fact that overall activity is insensitive to Cr loading makes it unlikely that further improvements could be achieved in the Cr/HTO catalysts.

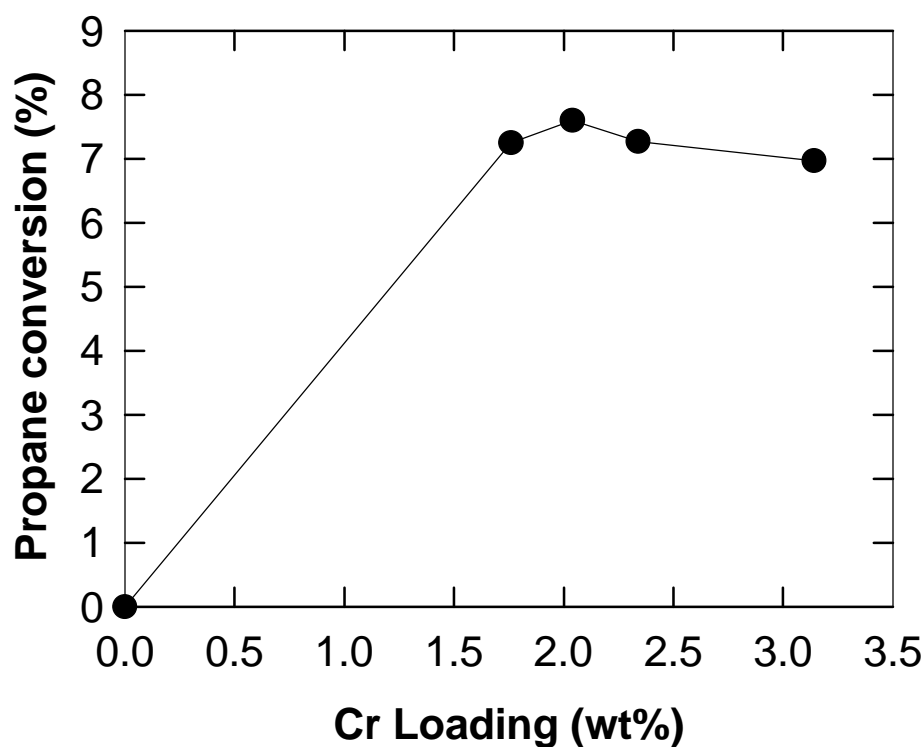


Figure 3: Propane dehydrogenation activity of Cr/HTO catalysts at 550°C, WHSV = 1.8 h⁻¹.

Comparison of the Cr/HTO catalysts with the commercial 7.5 wt% Cr/ γ -Al₂O₃ is also unfavorable. The commercial catalyst achieved an equilibrium limited propane conversion of ~30% with a selectivity of 83-90% at 550°C and a WHSV of 1.7 h⁻¹. Increasing the WHSV to 3.1 h⁻¹ resulted in only a slight drop in conversion to 26%, and a selectivity of 95%. Thus, the commercial catalyst is clearly more active than the Cr/HTO catalysts, and the inability to increase the activity of the Cr/HTO catalysts through increased metal loading leads to the conclusion that Cr/HTO catalysts are unlikely to provide any benefit over currently available technology. The Cr/HTO catalysts do, however, show slightly improved selectivity relative to the commercial catalyst but this advantage is not sufficient to overcome the low activity.

Platinum Catalysts

Characterization

Table 1 summarizes the physical properties of the various silica and alumina aerogels and xerogels. Note that three different syntheses were performed for each sample using nominally

Table 1: Physical properties of silica and alumina aerogels and xerogels

	Silica Xerogel	Silica Aerogel	Alumina Xerogel	Alumina Aerogel	Silica Xerogel *
Pt Content (wt%) (3 samples)	0.31 0.25 0.15	0.26 0.27 0.15	0.37 0.10 0.20	0.26 0.10 0.37	0.25
Surface area of powders (m ² /g) ^a	1295	1333	440	627	643
Surface area of -60/+80 mesh fraction (m ² /g)	739	670	468	336	— ^b
Surface area after reaction (m ² /g)	645	260	439	228	697
weight loss at 400°C (%)	50	65	60	65	18 ^c
Metal particle size by TEM (uncalcined) (nm)	1.5	1.5			2.0
Metal particle size by TEM (calcined) (nm)	4.5	4.0	3.5		3.5
Metal particle size from H ₂ chemisorption (nm)	4.5		4.9		2.5

a) Surface area of as-prepared powders after calcining to 400°C.

b) No -60/+80 mesh fraction was obtained from the Pt/silica xerogel* sample.

c) Weight loss measured after heating to 600°C.

the same procedure. The resulting platinum loadings are highly variable, indicating that the Pt loading is sensitive to small variations in procedure. We believe that a major factor in determining the Pt loading is the length of time allowed between addition of the LiBH_4 reducing agent and addition of the gelling agent (TBAOH for silica and HNO_3 for alumina). Longer intervals seem to increase the Pt loading by allowing more complete reduction of the PtCl_2 prior to gelation. While the Pt loading varies significantly among the samples, the other physical properties listed in table 1 are relatively invariant with Pt loading.

Initially, TEM shows the presence of small Pt particles (<2 nm) for all of the samples. With one exception, thermal gravimetric analysis (TGA) of the samples indicates a total weight loss of greater than 50%, primarily due to the oxidation of residual organic matter within the gel matrix. This weight loss is essentially complete by 450°C for all of the samples except the Pt/silica xerogel*, which loses only 18 % of its original weight after heating above 600°C . Following the thermal treatment, the surface areas of all of the samples are quite high. The reported surface areas represent a dramatic increase over the surface areas of the as-prepared materials, which are typically less than $5\text{ m}^2/\text{g}$. Note that the -60/80 mesh fractions generally possess lower surface areas than the powders. This result likely indicates that the more mechanically sound portions of the monoliths, which are most likely to be retained in the -60/+80 mesh fraction during grinding, possess a lower surface area than the weaker sections of the monolith. In addition to influencing surface area, the thermal treatments also result in some Pt particle growth, with final particle sizes approximately twice the original sizes. The Pt/silica xerogel* sample exhibits the greatest resistance to Pt particle growth, particularly when the hydrogen chemisorption results are considered.

Propane Dehydrogenation

The platinum samples were tested for propane dehydrogenation at 550°C and results are given in table 2. Note that the WHSV's and pretreatment conditions differ significantly among the six samples studied. The variation in WHSV arises from two factors. First, the samples changed in volume and weight during activity testing making it impossible to set a precise WHSV *a priori*. Second, for some samples, particularly the calcined Pt/silica xerogel*, the amount of sample available was very small and limitations in mass flow controller range did not allow the WHSV to be decreased sufficiently to achieve the desired value. Variations in pretreatment conditions arose from the need to experiment with various pretreatments to determine the optimum activation conditions. Thus, for samples tested first (Pt/silica xerogel and Pt/alumina aerogel), it had not been realized that hydrogen reduction is advantageous, while for later samples the beneficial effects of hydrogen reduction had been discovered and were utilized to maximize activity. Because of these variations, fair comparison of the various catalysts cannot be made, and the results can only be used to demonstrate the potential of this class of dehydrogenation catalysts.

Based on the results presented, it is clear that the Pt/silica xerogel* obtained the best performance of any of the catalysts. Given the very high WHSV for the calcined Pt/silica xerogel*, the initial conversion of 12.7% is especially impressive. Note, however, that this catalyst deactivates extremely quickly and severely. Thus, balancing activity and stability points to the uncalcined Pt/silica xerogel* as the most favorable sample to evaluate the potential of these catalysts. The propane conversion of 12-15% over this catalyst is approximately half that obtained over the commercial 7.5 wt% Cr/alumina catalyst. Note, however, that the WHSV was

35% greater for the Pt catalyst, and that the activation parameters have not yet been exhaustively explored for any of the Pt catalysts. Given these two factors, the performance of the Pt/silica xerogel* catalyst is quite promising, and is certainly worthy of further exploration.

Table 2: Propane Dehydrogenation Activity of Pt Catalysts

Sample	WHSV (h^{-1})	Pretreatment Conditions	Propane conversion (%) ^a	Propylene Selectivity (%) ^b
Pt/Silica Xerogel	7.0	None	1.3-1.1	85
Pt/Silica Aerogel	6.7	Air, 10 min., 550°C H ₂ , 10 min., 550°C	6.9-1.5	47-90
Pt/Alumina Xerogel	5.7	Air, 10 min., 550°C H ₂ , 10 min., 550°C	7.8-6.7	80-85
Pt/Alumina Aerogel	6.5	Air, 10 min., 550°C	5.4-2.8	83-92
Pt/Silica Xerogel* (Uncalcined)	4.2	H ₂ , 10 min., 550°C Air, 10 min., 550°C H ₂ , 10 min., 550°C	15.7 - 12.3	63-90
Pt/Silica Xerogel* (Calcined 600°C)	17.1	H ₂ , 10 min., 550°C	12.7-4.7	71-94

- a) Propane conversion generally decreased with time. Run times were generally on the order of 30-40 minutes.
- b) Propylene selectivities generally increased as conversion decreased.

CONCLUSIONS AND RECOMMENDATIONS

The relatively poor propane dehydrogenation performance of Cr/HTO catalysts relative to commercial Cr/Al₂O₃ catalysts now appears to be due to a fundamental limitation of the Cr/HTO technology. It is possible that with more detailed characterization of the Cr/HTO catalysts, a better understanding of the factors leading to the poor performance could be achieved and used to improve the Cr/HTO performance. Given the difficulties and inherent uncertainties in such an undertaking, continued investigation of the Cr/HTO system seems unwarranted.

In contrast, the results for platinum particles supported on silica and alumina aerogels and xerogels are quite promising. Without optimizing synthesis parameters or conducting a detailed study of catalyst activation methods, relatively high propane conversions have been achieved with good selectivities. Through variation of catalyst synthesis procedures and systematic studies of catalyst pretreatment, it is highly likely that substantially better performance can be achieved with these materials. Performance approaching or exceeding that of existing commercial catalysts would be the ultimate goal of such studies.

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